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WIRES water

Article type: Overview

On the importance of very long-term water quality records

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Abstract

This overview is concerned with the value of long-term records of water quality in river basin management. In a world where change rather than stasis is increasingly the norm, monitoring is an essential way to discover whether there are significant undesirable changes taking place in the natural environment. The regular collection and processing of information involves systematic and purposeful observation, a deliberate plan of action in which the data have considerable value given knowledge of their context in time and space. Long-term data reveal important patterns, which allow trends, cycles and rare events to be identified. This is particularly important for complex systems where signals may be subtle and slow to emerge. Moreover, long-term data sets are essential to test hypotheses undreamt of at the time the measurements were started. The overview includes long time series from UK rivers showing how water quality has changed over time – and continues to change. An important conclusion is the long time frame of system recovery, well beyond the normal lifetime of individual governments. At a time of increasing hydroclimatic variability, long time series of water quality observations remain critically important; continuity of observations is critical at key benchmark sites.

Introduction

London's water supply reached crisis point in the mid 19th century with outbreaks of cholera and other problems arising from extraction of water from the polluted River Thames or from contaminated springs and well within the city. The Metropolis Water Act 1852 made "provision for securing the supply to the Metropolis of pure and wholesome water." Water filtration was made compulsory and new water intakes on the Thames were established upstream of London, above the tidal limit at Hampton, by the engineer, Joseph Quick, paralleling the new sewer system that was being created by Sir Joseph Bazalgette. The cholera outbreak of 1854, during which John Snow famously identified the source of the outbreak as the public water pump on Broad Street, confirmed that the Act was not a moment too soon. The relevant point here is that, not only was a new drinking water supply constructed, but a monitoring programme was instigated to test river water quality on a regular basis, to ensure it was satisfactory for abstraction or, conversely, to detect unwelcome changes. These are some of the earliest water quality measurements ever made¹; systematic and independently verifiable data are available from 1868². Figure 1 shows, by way of example, the continuous monthly record of average nitrate concentrations for the Thames at

Hampton, the longest continuous record of water chemistry available anywhere in the world³ (Howden et al., 2010).

Why “monitoring” is important

Among its definitions of the word *monitor*, the Oxford English Dictionary includes “something that reminds or gives warning” and “keep under systematic review”. Monitoring is not just about making measurements: it is increasingly recognised that the data must be made available. Reporting of results entails giving feedback and, moreover, enables the gathered information to be used in management decisions. The implication is that, whereas the original monitoring programme may simply have been designed to provide regular, routine observation, the information collected can nevertheless come to form the basis for catchment management plans to improve river water quality. Thus, as well as the detection of episodes of poor water quality, the identification of insidious, undesirable changes becomes an equally important outcome of ongoing surveillance.

In scientific terms, routine monitoring was traditionally regarded as low-grade activity, but in recent decades a more positive view has emerged, acknowledging that the regular collection and processing of information involves systematic and purposeful observation, in other words a deliberate plan of action. Long water quality time series are important for a number of reasons^{4,5}:

1. Long-term data reveal important patterns for scientists to explain, allowing trends, cycles and infrequent events to be identified. This is particularly important for complex systems where signals may be subtle and slow to emerge. Subtle processes are embedded within highly variable systems so that their weak signal cannot be extracted from a noisy background without a long record. Relatively short time series (i.e. < 10 years) tend to be highly influenced by inter-annual hydroclimatic variability, such that long-term trends are often obscured⁶.
2. It follows that long records provide the context within which shorter data sets, including those obtained from short-period field experiments, can be interpreted⁷.
3. By definition, rare events occur infrequently; long time series are more likely to include them, providing evidence of event itself and the context within which the event may be evaluated. Long records can also afford the basis for judging whether a very rapid shift in behaviour is exceptional or a normal component of system variability.
4. Long-term data sets are essential for testing hypotheses undreamt of at the time the measurements were started. It is remarkable how often variables, of no great significance within the original monitoring scheme, suddenly become the focus of attention as new and often urgent questions emerge.
5. As computer modelling becomes ever more dominant, it is increasingly recognised that models are only as good as the data used to calibrate and verify them. The continued need for reliable data implies a requirement to maintain monitoring networks, in particular benchmark stations with exceptionally long records.
6. Monitoring is an essential way of discovering whether there are significant undesirable changes taking place in the natural environment. As noted above, this was often not the original justification for monitoring programmes, which were generally established to signal acute episodes rather than chronic change. Some scientific programmes like the Long Term

Ecological Research Network (LTER: USA) and the Environmental Change Network (ECN: UK) have been deliberately established with change in mind.

Some long time series and their interpretation

The continuous monthly record of average nitrate concentrations for the Thames at Hampton since 1868 (Figure 1) shows a clear seasonal cycle; there are higher concentrations during winter when soil leaching processes are operating⁸. However, of more interest is the long-term pattern, emphasised on Figure 1 by the running mean. Nitrate concentrations rose during World War II and then stabilised at almost double their previous level. There was a further step-change in the early 1970s, when average concentrations jumped from around 4 mg/l to almost 8 mg/l and, in common with the earlier increase, these concentrations have remained stubbornly high despite policy-driven interventions to reduce catchment nitrogen inputs since the early 1980s, in particular the EU Nitrates Directive (91/676). Immediate increases indicate near-stream and shallow subsurface runoff sources in parts of the catchment, whereas the sustained shift in mean concentration reflects long-residence time groundwater pathways. A two-reservoir transfer function model can be used to identify nitrate export associated with surface and groundwater pathways⁹. Results indicate that the response time of the Thames catchment is of the order of decades, given the delays induced by groundwater flow through the main aquifers. This implies that any attempt to return nitrate concentrations to levels prevailing in the late 19th Century would require extreme changes in land use and land management. By definition, any policy solution must also have a time frame of several decades, much longer than the 5-year maximum term for UK governments, more akin to the EU's Water Framework Directive, enacted in 2000 with a target date of 2015¹⁰. As the Environment Agency for England and Wales comments on its website: "We cannot create a better water environment overnight."

Figure 2, which plots monthly means of water colour, a proxy for dissolved organic carbon (DOC), for the River Tees, UK¹¹, shows how perspectives change as the record lengthens. The record for a single year is not instructive, yet this is often the timescale for PhD fieldwork; there is limited context for field experiments therefore. As the record lengthens, seasonal cycles become apparent and gradually the scale of inter-annual variability emerges. Sometimes unusual or rare events are included, in this case the extreme drought of 1975-76 and a post-drought period of apparently enhanced concentrations. This raises questions about leaching processes in the peat-covered headwaters during and after a very dry period: does the record simply show the result of more leaching in the wet post-drought years or has there been structural change to the peat soil which alters the leaching processes in a more fundamental way? If the latter, are the changes permanent or does the peat eventually recover? An intriguing linear trend is only apparent in a long record spanning several decades. In this hydroclimatic setting, it seems that anything less than about 12 years simply indicates the result of climatic variability; trends can be more reliably identified as the series lengthens and climatic noise becomes relatively less important⁶. Records of at least 10 years in length for 315 sites across Great Britain were used to study trends in DOC¹²; 216 showed a significant increase consistent with trends in air temperature and atmospheric CO₂. Questions remain about the carbon cycling processes in peat that generate DOC inputs to river systems and about the role of other potential drivers such as atmospheric sulphur deposition or the legacy of drought episodes. Thoughts of anthropogenic climate change and its impact on fluvial

systems were hardly in the minds of those who set up the water colour monitoring on the Tees in the early 1970s; their sole concern was drinking water quality. It is nevertheless fortunate that such records, produced for quite another purpose, can be utilised to address emerging questions of global significance. At the same time, whatever the implications of increased DOC export in rivers, a doubling of DOC concentrations has meant a significant increase in treatment costs for water supply companies. One possible response has been to consider whether a different approach to the management of peat-covered headwater catchments might provide a means of arresting the increase and even reversing the trend. Thus, a water supply company might well use monitoring data at two very different time scales: for short-term (hours, days) control of drinking water quality and for long-term (years, decades) strategic planning of water resources.

Of course, long water quality time series are of little use without accompanying hydrometric data, especially if flux (also known as load, the total amount exported per unit time) needs to be calculated. Very long precipitation records are not unusual but long records of river flow are less common, especially for lower-order tributaries. Figure 3 shows river discharge and nitrate flux to the Wash estuary on the east coast of England. Nitrate fluxes pre-1957 are based on nitrate concentrations from the River Stour, a river in the same region⁷. Since the general pattern of nitrate concentrations for rivers draining to the Wash resembles that shown for the Thames in Figure 1, it is not surprising that nitrate fluxes increase sharply from the 1960s to peak in 1977, a very wet year following the 1975-76 drought. Thereafter, fluxes have only declined very gradually. Higher fluxes occur in wetter years, but there is no discernible trend in river flow across the period. Note that annual nitrate-nitrogen flux first exceeded $20 \text{ kg ha}^{-1} \text{ y}^{-1}$ in the 1977 water year (begins 1/10/76); this is the upper threshold for nitrogen (N) flux for catchments “moderately influenced by human activity”¹³. Including 1977, this level has been exceeded in 11 of 31 years since then. Hessen’s lower threshold is $8 \text{ kg N ha}^{-1} \text{ y}^{-1}$: in the 28 years up to 1965, 20 years fell below this level; this threshold was first exceeded in 1940, during WWII, when much grassland was ploughed to grow arable crops. 1997 was the most recent year when nitrogen load fell below this lower threshold. Figure 3 thus illustrates the magnitude of the change in nitrate fluxes to the Wash estuary over the last half century – from a low to a high level of human impact, mostly generated by intensification of agriculture^{9,14}.

Emerging themes and concerns

As well as revealing evidence of change, long water quality records may well contain evidence of changing variability too. We are told that “stationarity is dead”¹⁵. There is plenty of evidence that hydroclimatic variability seems to be increasing^{16,17,18}, whilst model-based forecasts of future climates suggest that hydroclimatic systems can only become more unstable. Non-stationary climate drivers must impact upon response variables, changing the nature and strength of feedback mechanisms and altering system resilience. Increased connectivity, often the result of land-use change (e.g. removal of riparian buffer zones or by-passing via under-drainage), may well increase vulnerability and decrease resilience of ecohydrological systems¹⁹. Strong seasonal contrast in hillslope inputs from hillslopes to riparian zones and thence to the stream^{20,21,22} naturally shifts the balance between nitrate attenuation and export²³ or, in other words, between *in situ* nutrient cycling and transport. However, there may be a permanent change in landscape connectivity, most likely as a result of the installation of land drainage, which can drastically alter flow paths and

residence times, linking hillslopes directly to the river and leaving riparian zones effectively isolated in between. No doubt natural landscapes differ in their sensitivity to change but human impact invariably seems to reduce the capacity of a system to resist change. With the removal of barriers to change, there is greater coupling between individual elements of the system and the consequent ability of the system to transmit matter and energy^{19,24}. Various changes in land use and land management might be employed in an attempt to reverse this trend of increased connectivity and thereby decouple landscape elements (e.g. re-introduction of crop rotations to reduce tillage frequency, installation of buffer zones) but, even if human disturbance in river basins can be minimised, increased hydrological variability seems inevitable as a result of externally-forced climate change and low-frequency climatic variability. Stationarity cannot be revived¹⁵.

There are, of course, limitations to traditional monitoring protocols: given the issue of aliasing, relatively infrequent sampling is bound to restrict our understanding of hydrological variability, allowing only a partial interpretation of system behaviour. This is why new measurement techniques based on state of the art electronics and mobile-phone telemetry offer such exciting prospects for high-frequency observations²⁵. Nevertheless, we concur that continuity of observations is critical¹⁵ and would argue for continued maintenance of traditional monitoring schemes, at least at key benchmark sites⁵. Currently, only a limited number of on-site techniques exist for continuous measurement, so continuity of record for many determinands can only be achieved by continuing to take water samples for subsequent analysis. In any case, until we can be fully confident about new equipment performance (accuracy and precision), it would seem wise to run old and new measurement methods in parallel. The following criteria for identification of benchmark monitoring sites have been suggested²⁶: homogenous, quality-controlled records; suitability for low-flow analysis including no appreciable direct human influence on river flow during low flow (e.g. major abstractions, reservoir storage); catchment area not exceeding 1000 km²; time series of at least 40 years. In relation to the last point, benchmark series should be unbroken or contain very few gaps. Even if a data series is found to be homogenous, this does not mean that the drainage basin is in pristine condition. For example, one study²⁷ claimed to have selected ten “near-natural” UK catchments not significantly impacted by human activity but in a UK context it is hard to imagine any basin entirely free of human interference. Probably the best one can do is to choose smaller rather than larger basins, not much affected by urban sprawl, reservoirs or major abstractions, where the runoff regime depends primarily on the relations between climate, vegetation, soils and rock structure²⁸. Even the most highly regarded sites will have their weaknesses: for example, the control catchments at Coweeta, time series started in the 1930s, were established only a few years after the destruction caused to the forest canopy by the chestnut blight fungus and low-impact burning, grazing and logging before that²⁹. Even today, these basins hardly constitute “old growth”, let alone in the 1930s. This is no criticism of these world-renowned experiments but it does remind us that about contingency: the influence of prior events on current system behaviour and the difficulty of defining initial conditions to be compared to later changes. The point is that, having established such “controls”, we should then seek to minimise subsequent change that might cause inhomogeneity; this is more easily managed in small, headwater catchments like those at Coweeta, of course. How perceptive can we be about what to measure at our benchmark sites? Since the new questions that will arise in the future cannot be anticipated, long-term monitoring can be perceptive, but never prescient⁴. In maintaining benchmark sites, there need be no specific questions in mind, merely a

firmly held belief in the importance of supporting well-established measurement programmes over long periods of time.

Notwithstanding the need to maintain certain key records, we should not be overly committed to maintaining existing monitoring sites at all costs. The important point is to measure the right thing in the right place at the right time. New sensors will allow new sampling strategies, capturing new patterns of variation in time and space. In the previous era of limited resources and costly laboratory analysis, there was an apparent contradiction; we could not understand catchment processes without monitoring and yet we could not establish a monitoring programme without understanding process. There is now a way out of this paradox, since recent research has provided better understanding of catchment systems; combined with new, relatively inexpensive measurement techniques, the time now seems ripe for new sampling strategies, delivering high-frequency information in time and space. Previous measurements were not always made in the best place, often constrained by where it was simplest (i.e. cheapest) to make measurements (e.g. at an existing water treatment works). We should now aim to implement campaigns that provide measurements where we need them. For example, central limit theorem means that solute concentrations in higher-order sections of a river network will tend to an average of low-order variability. We would learn more by installing a network of measurement probes across a wide range of first-order tributaries in order to be able to identify hot spots and hot moments of process activity^{19,30,31}. Such campaigns should be time-limited, replaced by new sampling strategies as new needs arise. Meanwhile, maintenance of a few benchmark sites will sustain the long records necessary for revealing subtle trends in noisy systems and warning of emerging unwelcome change.

At a time of increasing hydroclimatic variability, how should research on water quality proceed? We have already noted the need for long-term monitoring to continue at key benchmark sites. Modelling can complement but never replace observations^{4,15}. Nevertheless, modelling is likely to be a key element in future research as we seek to understand how hydroclimatic drivers affect response variables. Another complementary approach involves the use of proxy data to allow us to extend records back beyond the period of instrumental records; a good example of a proxy record for a climatic driver is the use of dendrochronology to provide evidence of medieval “mega-droughts” in the western United States^{32,33}. We have some capability to use proxy records of water quality: for example, using past records of land use to estimate input loadings using export coefficient models⁹ or the use of microfossils in lake sediment cores to document changes in lake water acidity over time³⁴. Of course, long time series of water quality observations remain critically important, whether being resampled to analyse for signs of non-stationarity or providing the basis for stochastic modelling to describe the temporal evolution of their probability density function¹⁵. We see a need for more sophisticated methods to detect change points in time series, not so much in relation to shorter-term climatic variability, more for major shifts in system behaviour. Homogenous records are a vital requirement; very long records in particular are likely to require homogenisation^{26,35}. Techniques are needed to identify significant shifts in a time series, to supplement more traditional approaches like double-mass curves³⁶ (Searcy and Hardison, 1960); this remains the focus of ongoing research (e.g. Howden et al., 2011b).

Conclusion

We live in an increasingly connected world, through the flow of materials, organisms and information, both within and between regions that may or may not be even close to one another³⁷. This is as true of river basins as of any other sector of the natural environment. Connectivity allows fine-scale processes to propagate and impact large areas (e.g. nitrate drainage from first-order basins reaching marine ecosystems) and broad-scale drivers to alter local ecosystems (e.g. through the effects of climate change)³⁶. How does hydroclimate affect response variables? What is the nature and strength of the feedback? Slow, insidious change can lead eventually to thresholds and non-linear response. This is why long-term monitoring remains as important as ever: to detect unwelcome changes at an early stage, allowing for societal strategies of risk mitigation or adaption to be developed, and hopefully avoiding potentially catastrophic impact on aquatic ecosystems.

References

1. Meybeck, M. (2005). Looking for water quality. *Hydrological Processes* 19, 331-338. doi:10.1002/hyp.5778.
2. Hamlin, C. (1990). *A Science of Impurity: Water Analysis in Nineteenth Century Britain*. University of California Press.
3. Howden, N. J. K., Burt, T. P., Worrall, F., Whelan, M.J. and Bierzoza, M. (2010). Nitrate concentrations and fluxes in the River Thames over 140 years (1868–2008): are increases irreversible? *Hydrological Processes*, 23, 2657-2662. DOI: 10.1002/hyp.7835.
4. Burt, T.P. (1994). Long-term study of the natural environment: perceptive science or mindless monitoring? *Progress in Physical Geography*, 18, 475-496.
5. Burt, T.P., Howden, N.J.K., Worrall, F. and McDonnell, J.J. (2011). On the value of long-term, low-frequency water quality sampling: avoiding throwing the baby out with the bathwater. *Hydrological Processes*, 25, 828–830. DOI: 10.1002/hyp.7961
6. Howden, N. J. K., Burt, T. P., Worrall, F. and Whelan, M.J. (2011a). Monitoring fluvial water chemistry for trend detection: hydrological variability masks trends in datasets covering fewer than 12 years. *Journal of Environmental Monitoring*, 13 (3), 514 – 521. DOI: 10.1039/c0em00722f
7. Burt, T.P., Howden, N.J.K., Worrall, F. and Whelan, M.J. (2008). Importance of long-term monitoring for detecting environmental change: lessons from a lowland river in south east England. *Biogeosciences* 5, 1529-1535. <http://www.biogeosciences.net/5/1529/2008/bg-5-1529-2008.html>
8. Burt, T.P., Arkell, B.P., Trudgill, S.T and Walling, D.E. (1988). Stream nitrate levels in a small catchment in south west England over a period of 15 years (1970-1985). *Hydrological Processes*, 2, 267-284.
9. Howden, N. J. K., Burt, T. P., Worrall, F., Mathias, S. and Whelan, M.J. (2011b). Nitrate pollution in intensively farmed regions: What are the prospects for sustaining high-quality groundwater? *Water Resources Research* 47, W00L02, doi:10.1029/2011WR010843.
10. Worrall, F., Spencer, E. and Burt, T.P. (2009). The effectiveness of nitrate vulnerable zones for limiting surface water nitrate concentrations. *Journal of Hydrology* 370, 21-28.
11. Worrall, F., Burt, T.P. and Shedden, R.M. (2003). Long-term records of riverine dissolved organic carbon. *Biogeochemistry* 64, 165-178.
12. Worrall, F. and Burt, T.P. (2007). Flux of dissolved organic carbon from U.K. rivers. *Global Biogeochemical Cycles* 21 (1), GB1013. doi:10.1029/2006GB002709.

13. Hessen, D.O. (1999). Catchment properties and the transport of major elements to estuaries. *Advances in Ecological Research* 29, 1-41.
14. Howden, N. J. K., Burt, T.P., Worrall, F., Mathias, S. and Whelan, M.J. (2013). Farming for Water Quality: Balancing Food Security and Nitrate Pollution in UK River Basins. *Annals of the Association of American Geographers* 103 (2), 397-407. DOI:10.1080/00045608.2013.754672.
15. Milly, P.C.D., Betancourt, J., Falkenmark, M., Hirsch, R.M., Kundzewicz, Z.W., Lettenmaier, D.P. and Stouffer, R. J. (2008). Stationarity Is Dead: Whither Water Management? *Science* 1 February 2008: 573-574. DOI:10.1126/science.1151915.
16. Burt, T.P. and Ferranti, E.J.S. (2012). Changing patterns of heavy rainfall in upland areas: a case study from northern England. *International Journal of Climatology*, 32: 518–532. DOI: 10.1002/joc.2287.
17. Laseter, S.H., Ford, C.R., Vose, J.M and Swift, L.W. (2012). Long-term temperature and precipitation trends at the Coweeta Hydrologic Laboratory, Otto, North Carolina, USA. *Hydrology research*, 43.6 890-901. DOI: 10.2166/nh.2012.067
18. Hannaford, J. and Buys, G. (2012). Trends in seasonal flow regimes in the UK. *Journal of Hydrology* 475, 158-174.
19. Burt, T.P. and Pinay, G. (2005). Linking hydrology and biogeochemistry in complex landscapes. *Progress in Physical Geography*, 29(3), 297-316.
20. Haycock, N.E. and Burt, T.P. (1993). The role of floodplain sediments in reducing the nitrate concentration of subsurface runoff: a case study in the Cotswolds, England. *Hydrological Processes*, 7, 287-295.
21. Burt, T.P., Matchett, L.S., Goulding, K.W.T., Webster, C.P. and Haycock N.E. (1999). Denitrification in riparian buffer zones: the role of floodplain sediments. *Hydrological Processes*, 13, 1451-1463.
22. Clément, J.-C., Aquilina, L., Bour, O., Plaine, K., Burt, T.P. and Pinay, G. (2003). Hydrological flowpaths and nitrate removal rates within a riparian floodplain along a fourth-order stream in Brittany (France). *Hydrological Processes*, 17, 1177-1195.
23. Ocampo, C. J., Oldham, C. E. and Sivapalan, M. (2006), Nitrate attenuation in agricultural catchments: Shifting balances between transport and reaction, *Water Resources Research*, 42, W01408, doi:10.1029/2004WR003773.
24. Brunson, D. and Thornes J.B. (1979). Landscape sensitivity and change. *Transactions, Institute of British Geographers* NS4(4), 463-484.
25. Kirchner J.W., Feng, X., Neal, C. and Robson, A. J. (2004). The fine structure of water-quality dynamics: the (high-frequency) wave of the future. *Hydrological Processes* 18: 1353–1359.
26. Stahl, K., Hisdal, H., Hannaford, J., Tallaksen, L. M., van Lanen, H. A. J., Sauquet, E., Demuth, S., Fendekova, M. and Jódar, J. (2010). Streamflow trends in Europe: evidence from a dataset of near-natural catchments. *Hydrology and Earth System Sciences* 14, 2367-2382.
27. Lavers, D., Prudhomme, C. and Hannah, D.M. (2010). Large-scale climate, precipitation and British river flows: Identifying hydroclimatological connections and dynamics. *Journal of Hydrology* 395, 242-255.
28. Burt, T.P. (1996). The hydrology of headwater catchments. In: G Petts & P Calow (eds), *River Flows and Channel Forms*, Blackwell, Oxford, 6-31.

29. Elliott, K.J. and Swank, W.T. (2008). Long-term changes in forest composition and diversity following early logging (1919-1923) and the decline of the American chestnut (*Castanea dentata*). *Plant Ecology* 197, 155-172.
30. Bishop, K., I. Buffam, M. Erlandsson, J. Folster, H. Laudon, J. Seibert, and J. Temnerud. (2008). Aqua Incognita: the unknown headwaters. *Hydrological Processes*, 22(8), 1239-1242
31. McClain, M.E., Boyer, E.W., Dent, C.L., Gergel, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., Harvey, J.W., Johnson, C.A., Mayorga, E., McDowall, W.H. and Pinay, G. (2003). Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems* 6, 301-312.
32. Cook, E.R., D.M. Meko, D.W. Stahle, and M.K. Cleaveland. (1999). Drought reconstructions for the continental United States. *Journal of Climate*, 12, 1145-1162.
33. Cook, E.R., C. Woodhouse, C.M. Eakin, D.M. Meko, and D.W. Stahle (2004). Long-term aridity changes in the western United States. *Science*, 306, 1015-1018.
34. Battarbee, R. W., Stevenson, A. C., Rippey, B., Fletcher, C., Natkanski, J., Wik, M. & Flower, R. J. (1989). Causes of Lake Acidification in Galloway, South-West Scotland: A Palaeoecological Evaluation of the Relative Roles of Atmospheric Contamination and Catchment Change for Two Acidified Sites with Non-Afforested Catchments. *Journal of Ecology*, 77, 651-672.
35. Burt, T.P. and Howden, N.J.K. (2011). A homogenous daily rainfall record for the Radcliffe Observatory, Oxford, from the 1820s. *Water Resources Research*, 47, W09701, doi:10.1029/2010WR010336.
36. Searcy, T.K. and Hardison, C.H. (1960). Double mass curves. *USGS Water Supply Paper* 1541-B, 66pp. United States Geological Survey, Washington D.C.
37. Peters, D.P.C., Groffman, P.M., Nadelhoffer, K.J., Grimm, N.B., Collins, S.L., Michener, W.K. and Huston, M.A. (2008). Living in an increasingly connected world: a framework for continental-scale environmental science. *Frontiers in Ecological Environments*, 6(5), 229-237.

Figure captions

1. Time series plot of monthly nitrate concentration (mg NO₃-N/L) for the River Thames at Hampton together with an approximate 12-month running mean (from Howden et al., 2010).
2. Observations of water colour (Hazen units) demonstrate the importance of a broad temporal perspective (based on Burt, 1994).
3. Annual nitrate flux (kg/ha N) for rivers draining into to the Wash estuary, eastern England. Also shown is the annual runoff (mm). Pre-1957 nitrate data are derived from the River Stour, an adjacent catchment.